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(57) 14 Claims

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The present invention rolates to a dontal hygiene device, as it were, or a photoelectric chemical reaction type capable of providing a dental hygiene offect through an exidation-reduction reaction caused when light energy is converted into electric energy satisfying four conditions: light, n-type semiconductor, water and teeth.

It is known in recent years that fluorine is advantageously affective for teeth; thus, some tooth pastes contain this fluorine.

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However, the surface of teeth, as being in contact with sputum having a lower pH value than tooth tissue, has characteristics preventing permeation of enions such as the fluorine, thereby suppressing the effect of the anions.

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Accordingly, there has been provided a method in which a battery or a general steetric power source is used and a negative electrode is provided at a portion of a tooth brush implanting a brush while gum is used as a positive electrode while using the fuman hedy as conductive means whereby an electrolytic reaction as expressed by the following formula is danced through sputum or drinking water.

2H+ + 20 ------ H2 (negative electrode)

thus;

H20 ----- 1/2 D2 + H2

Thus, the permenting of the enions such as fluorins into the tooth tissue is promoted.

However, in the case of this method, since the human



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body having considerable electric resistance is used as a portion of circuit, relatively large electric power is necessary for causing the above reaction. There is also another disadvantage that the electric current needed for the reaction often fails to flow due to a difference in reistance depending on the individual. If a high voltage is employed for overcoming the above difficulty, there occurs business health basard.

The present invention provides a dental hygiene device which overcomes the aforementioned prior-art disadvantages and which is capable of effectively contributing to improved dental hygiene preventing decalcification of tests due to decrease in parable and preventing tooth cavity or pyorrhes through decomposition of dental plaque or deposited pigment.

According to the invention, the dental hygiene device comprises a body including an inserting portion to be inserted into the mouth and placed to react with water and/or sputum and a grip portion to be exposed out of the mouth and an n-type semiconductor accommodated in the body and adapted for causing photocatalyst reaction as at least a portion thereof is inserted into the mouth to come into contact with water and/or sputum, the n-type semiconductor being formed as a thin layer on a surface of a conductive member. Suddebly-said thin layer n-type semiconductor formed on the surface of the conductive member has a thickness steeler than 1 N m.

Preferably said n-type semiconductor is obtained as semiconductor powder used as a way material therefore is treated by a method selected from the group including a pressure moulding, sintering, CVD, vacuum deposition, sputtering and ion plating. Preferably said inserting portion is formed separately from said grip portion so as to be detachable from the same. suitably said n-type semiconductor has a leading edge thereof toward said inserting portion disposed adjacent a brush provided at said inserting portion.

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What the prosent invention essentially differs from the prior art is as follows. In contrast to the prior-art in which a high voltage is needed for causing the exidation-reduction reaction, according to the present invention, since the semiconductor is employed for causing the photoelectric chemical reaction, an advantageous effect may be obtained even without using electric power. The present invention is also advantageous, as particularly described later, in that even in the case of using electric power in combination a sufficient effect may be obtained with a low voltage which does not pose whatever human health hazard.

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In this specification, it is to be noted, the exidation means removal of electron from a cortain matter and reduction means acceptance of electron.

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The present invention provides a denial hygiene device, comprising: a body having an inserting portion disposed to be inserted into a mouth and to respond to water and/or sputum; and an n-type semiconductor accommodated in said body and adapted for causing a photoelectric chemical reaction as being at least partially inserted into the mouth to come into contact with the water end/or enutum; a direct current source disposed in said body and connected to said semiconductor; and a good conductor disposed in said body and concected to said semiconductor; wherein, as said inserting portion is inserted into the mouth, said n-type semiconductor, said direct current source and said good conductor act together with to constitute a circuitry. Suitably said good conductor comprises a metal having a good corrosion resistivity. Profesably said metal having a good corrosion resistivity is selected from the group including stainless steel, Ti, Ti alloy, Al alloy, precious metals and procious metal alloys. Suitably said n-type semiconductor is selected from the group including TiO2, ErO2, Fe2O3. Desirably said n-type semiconductor is selected from the group including TlO_2 , ZrO_2 , Fe_2O_3 .

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The present invention will be described in greater detail hereinafter with reference to the accompanying drawings in which:

Fig. 1 is a partially cutout front view showing one embodiment of a dontal hygiene device related to the present invention,

Fig. 2 is a view illustrating the principle of the dental hygions device related to the present invention.

Fig. 3(a) and Fig. 3(b) are respectively a partially cutout front view showing enother embodiment of the dental hygiene device related to the present invention and a vertical section of the device shown in Fig. 3(b).

Fig. 4 is a view illustrating the principle of the dental bygiene device related to the present invention,

Fig. 5 is a partially cutout front view showing still another embodiment of the apparatus related to the present invention,

Fig. 6 is a partially cutout front view showing a further embodiment of the device related to the present invention, and

Fig. 7 is a partially cutout front view showing a still further embodiment of the dental hygiene device related to the present invention.

As shown in Fig. 2, when light strikes the n-type semiconductor 4 exposed from the mouth, the n-type semiconductor acts as photocatelyst to cause a photocoloctric chemical reaction. More particularly, when the n-type semiconductor 4 formed on a surface of a conductive member is exposed to the solution, a

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difference between a Fermi level of the n-type semiconductor and exidation-reduction electric potential of the solution results in a formation of schottkey borrier on the surface of the n-type semiconductor, causing inwardly of the semiconductor a potential gradient, i.e. a deflection of band, whereby a space-charge layer is formed. If light $\{h \ \mathscr{N}\}$ is illuminated thereon, electron of valence band is excited into a conduction band thereby forming a positively charged hate p^+ in the balance band and excited electron e^- in the conduction band, whereby

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there occurs an exidation reaction on the illuminated surface in which the electron is removed from a substance in the solution. For example, on the surface of the semiconductor, electron is removed from Mr O molecule thoroby generating a highly active OH radical. This ON radical is capable of decomposing organic acid such as lattic acid which is conceived to be direct cause of dontal plaque leading to pyorrhea or of deculcification of tooth and the radical is also capable of eliminating deposited pigment.

On the other hand, the excited electron a "in the conduction band is moved by the potential gradient of the space-charge layer into the somiconductor body and then proceeds to a back thereof (a vicinity of teeth) wherehy there occurs a roduction reaction for supplying electron to the substance in the solution, thus contributing to the oral hygieno. This reaction is, for example, production of R_2 with disappearence of H . In this case, to be more specific, the ntypo semiconductor 4 is formed as a thin a type semiconductor layer to on a conductive member 4b formed of metal and the like. Accordingly, the excitod electron in the conduction band moves insade the conductive member 4b before disappearing as being re-combined with the hole in the valence band inside the somiconductor body, thus the reduction reaction

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For supplying the electron to the substance in the solution is caused efficiently. It is to be noted become that the sourconductor layer 4a on the surface of the conductive member 4b should be as thin as possible, preferably as this as 1 pm because of the following reason. If the semiconductor layer 4a has a short thickness, it is possible to form substantially flat the schottkey barrier to be formed on an outer surface of this layer 4a whereby it becomes easier to supply the electron to the substance in the solution and consequently the efficiency of the reduction reaction may be onhanced.

Also, it is conceivable to form the dental hyghene device not only of the n-type semiconductor attached to the body but also of a direct current power source and of a good conductor, these as a whole acting as a circuit when inserted into the mouth to become active.

Because of the difference between the exidationreduction electric potential of the solution and the
Permi level of the n-type comicconductor, there is
formed the Schotckey barrier on the surface of the ntype semiconductor, counting the potential gradient,
i.e. the deflection of band inwardly of the
semiconductor body, whereby the space-charge layer is
formed maintaining energy equilibrium. In this

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condition, if light is illuminated thereou, as shown in Mig. 4, the light excitation causes an excited electron e in the conduction band and a hole pt in the valence band. This excited electron of moves into the semiconductor, then further into a metal 'B' and finally reaches a scoth 'D' by way of a human body, causing a reduction coaction on a surface of the tooth 'u'. For instance, the electron having reached the tooth 'D' reduces H' heading to decalcification of the tooth thereby to gonorate Na. This means that it is possible to neutralize of lowered by dental plaque attached to the tooth Chereby advantageously preventing the decalcification of booth resulting from a decrease in pH value. In this way, a circuit is formed having as its opposite electrods the booth 'D' by way of the human body 'C'.

On the other hand, the hole p* caused in the valence band gets electron from the water in the solution thereby causing an exidation reaction. For example, on the surface of the semiconductor, the hole p* gets electron to produce highly active OK radical. This OK radical is capable of decomposing organic neid such as lactic acid which is conceived to be direct cause of dental plaque leading to pyerrhea or of decalcification of booth and the radical is also capable of eliminating deposited pigment. Such effect

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is also conspicuous for S. mutans which is conceived to be backeria responsible for booth cavity, thereby very effectively carrying out on the whole prevention of tooth cavify or pyorchea and beautification of footh. In this case, it is to be noted, if the n-type Semiconductor is constituted by substances such as TiO, and is not connected to the direct current source, the energy level in the valence band is considerably positivo providing strong oxidation effect; however, since the energy level in the conduction band is not so nogative, the reaction efficiency is not so high. according to the present invention, however, since the notype semiconductor is connected to the direct current source, the energy level in the conduction band may be sufficiently magazive. As a result, if is possible to promote the exidation-reduction reaction bhoroby to enhance the efficiency of the photoeloctric chemical reaction. That is to say, the connection of the semiconductor to the direct current source serves to promote the reduction roaction on the tooth surface and as a result to further enhance the exidation neaction of the semiconductor. ...

As described above, the combination of the metal 'B' in chair contact with the semiconductor and the direct current source 5 helps to promute the exidation-reduction reaction in the mouth. Therefore,

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compared with the conventional dontal hydrene device using a battery and the like, a high voltage source which may be detrimental for human health is not necessary.

In this case, it is to be noted, the n-type semiconductor need not necessarily be formed as the thin layor shown in Fig. 2.

The light needed for exciting the n-type semiconductor in this invention compaises natural light such as sun light or artificial light such as electric light. Therefore, the dental hygiene device according to the present invention is capable of effectively proventing tooth cavity, pyorrhea and the like without providing any detrimental effects for the human body.

Professed embodiments of a dental hygiene device will now be particularly described with seference to the accompanying drawings.

As shown in Fig. 1, a tooth brush body 3 formed in general of synthetic resin and the like is essentially constituted by an inserting portion partially implanted with brush is and by a grip

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portion 2 to be exposed out of the mouth. Inside the body 3, there is insertedly provided an n-type semiconductor 4 of a narrow width extending from the inserting portion 1 to the grip portion 2, a thin semiconductor layer 4a being formed on a surface of the n-type semiconductor 4. The width of this n-type semiconductor 4 should be so predetermined as to permit the semiconductor 4 to be accommodated in the body 3 and in this embledment the sumiconductor 4 has a linear configuration having a width of approximately The n-type semiconductor 4 may also have a narrow strip configuration. The n-type semiconductor 4 used in this emobudiment was formed by red-hosting at 1200 to 1500°C for one or two minutes a rd having a bar like shape with its diameter 3 mm and its length 50 mm and having a purity of 99.4 W, thereby producting TiO2 .

Figs. 3(a) and 3(b) show a tooth brush as another embodiment of the dental hygiens device related to the present invention. This tooth brush also includes an n-type comiconductor providing photoelectric effect. This n-type semiconductor 4 has its one end connected to a metal TI as a good conductor 6 chair-contactable with the semiconductor. Between the good conductor 6 and the semiconductor, there is inserted a battery acting as a direct current source 5.

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Further, inside the body 3 of the dental hygiene device shown in Fig. 1 and Figs. 3(a) and 3(b), there is formed a groove for catching water. And, the photoelectric chemical craction is effectively promoted through the water deposited in the groove 7. In the case the semiconductor 4 is formed transparent, substantially the whole of the semiconductor 4 may be inserted into the mouth with only a side portion thereof being exposed to the outside. Further, it is also possible to dispose a side leading edge of the inserting postion 1 of the semiconductor 4 shifted from the postion shown in Fig. 1 and Fig. 3(a) toward the vicinity of the brush 1a. With this arrangement, the photoelectric chemical reaction of the semiconductor 4 acts more effectively on the teeth.

The semiconductor 4 may be constituted, in addition to TiO, also by ETO, Fe_D, and the like. In short, any semiconductor may be used which is capable of producing sufficient photoelectric current in response even to natural light. Also, the semiconductor may be formed in any other fashion than that described becombefore. For example, positived Ti, Ar, Fe and the like is sintered at a high temperature or plute-shaped Ti, Ar, Fe and the like is treated by electrolytic exidation, thereby producing TiO, ArO,

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seminonductor used as a raw material may directly undergo process, or a semiconductor layer may be formed on an appropriate base plate by a CVD method, a vacuum deposition method, a sputtering method, an ion plating method and the like.

On the other hand, if the surface of the summonductor bears a metal which is a good nonductor, it becomes easier to cause the reduction reaction on the surface of the semiconductor. Repectally if a precious metal such as Pt is employed as the metal bound on the surface, the metal acts like a cutulysis in response to generation of hydrogen to increase the effect in the mouth. Also, even if any other metal than Pt such as Pd, Au, Ag or a combination thereof or Ti or Ti alloy and the like is employed, the effect is cohunced compared with the case when the semiconductor alone is employed.

The good conductor 6 may comprise, in addition to Ti, various kinds of stainless stool, Al alloy, Ag and Ag alloy and others.

The configuration of the body J may be conveniently moxified; thus, the present invention is not limited by the one shown in the accompanying drawings. For example, in the case of the body 3 shown in Fig. 1 and in fig. 3(a), the brust 1a may not

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be needed. In this case, the booth are washed, e.g. by washing liquid jetted from a portion of the body.

Pig. 5 shows a tooth brush as another embodiment of the dental hygiene device related to the present invention. In the case of this tooth brush, a compact semiconductor 14 is attached to the grip portion 2 and a conductive line 8 is extended therefrom to the inserting portion 1, thursby forming a conductive passage.

- 10 Fig. 6 shows a tookh brush as still another embodiment of the dental hygiene device related to the present invention. This tooth brush has a water-depositing groove 9 in place of the conductive line 8 shown in Fig. 5.
- Fig. 7 shows a tooth brash as a further embodiment of the dental hygione device related to the present invention. In this case, a body 13 is used as a conductive passage as being formed of a conductive material (onhacmful for the human body).

Figs. 5 through 7 show embodiments of the dontal hygiene device having a semiconductor, a direct current source and a conductive member. In place of these, the device may have a thin layer type semiconductor without using the direct current source.

Further, the inserting portion 1 may be formed separately from the grip portion such that the

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disserting portion 1 may be detachable from the latterwith this arrangement, even if the brush 1a implanted in the inserting portion 1 may wear due to use, the tooth brush may be repeatedly used by replacing only the inserting portion 1 without throwing away the whole tooth brush. In addition to this economic meets, this arrangement may provide another advantage of convenience since it becomes easier to clean the surface of the semiconductor.

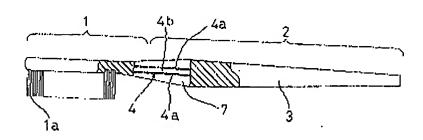


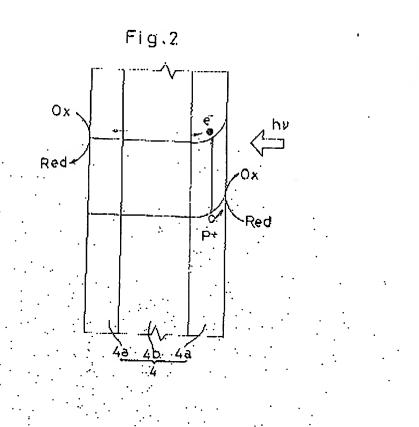
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à dental hygiune davico haviny a body with an insarking portion disposed to be inserted into a mouth and to respond to water and/or sputum and an n-type semiconductor accommodated in the body and adapted for causing a photocatalyst reaction as being at least particully inserted fato the mouth to come into contact with the water and/or sputum, the π -type somiconductor being formed as a thin layer on a surface of a conductive member, And, a dontal hyglene device having a body with an inserting portion disposed to be inscribed into a month and to respond to water and/o.c sputium and an n-type semiconductor accommodated in the hody and adapted for causing a photoelectric chamical reaction as being at least partially inserted into the wouth to come into contact with the water aud/or spullum, a direct current source disposed in the body and connected to the semiconductor and a good conductor disposed in the body and connected to the somiconductor. As the inserting portion is innerted Into the mouth, the n-type semiconductor, the direct current, source and the good conductor act Logetherwith to constitute a circultry.

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Fig.1





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Fig.3(a)

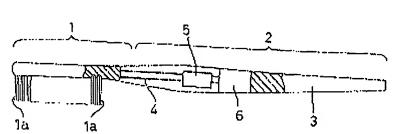
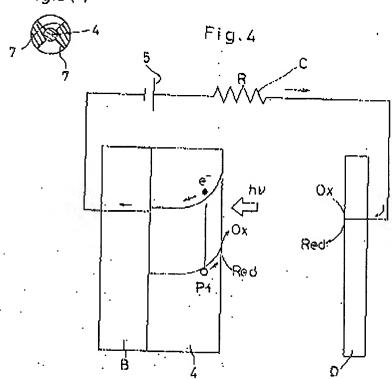


Fig.3 (b)



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Fig.5

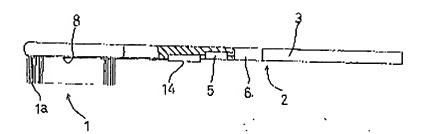
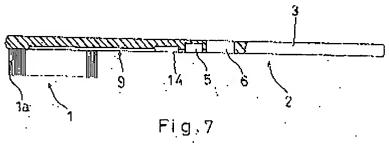
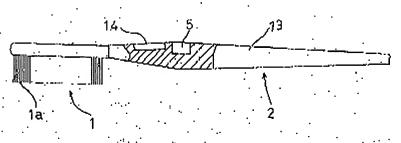


Fig.6





THE EMECUTARITY OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

- 1. A dental hygiene device, comprising: a body having an inserting portion disposed to be inserted into a mouth and to respond to water and/or aputum; and an n-type semiconductor accommodated in said body and adapted for causing a photocatalyst reaction as being at least partially inserted into the mouth to come into contact with the water and/or sputum; said n-type semiconductor being formed as a thin layer having a thickness less than 1 Aug on a surface of a conductive member.
- 2. A dontal hygione device, comprising: a body having an inserting portion disposed to be inserted into a mouth and to maspond to water and/or sputum; and an n-type semiconductor accommodated in said body and sdapted for causing a photoelectric chemical reaction as boing at least partially inserted into the mouth to come into contact with the water and/or sputum said n-type semiconductor being formed as a thin layer having a thickness less than 1 acm on a surface of a conductive member; a direct current source disposed in said body and connected to said semiconductor; and a good conductor disposed in said body and connected to said semiconductor; wherein, as said inserting portion is inserted into the mouth, said n-type semiconductor, said direct current source and said good conductor act together to constitute a circuitry.
- 3. A dental hygiene device, as claimed in claim 2, wherein sold good conductor comprises a metal having a good corresion resistivity.
- 4. A dental hygiene davice, as claimed in claim 3, wherein said metal having a good corrosion resitivity is selected



from the group including stainless steal, T1, T1 alloy, A1 alloy, precious metals and precious metal alloys.

- 5. A dental hygieno device, as claimed in claim 1, wherein said n-type semiconductor is selected from the group including TiO2, ZrO2, We2O3.
- 6. A dontal hygiens device, as claimed in claim 2, wherein said n-type semiconductor is selected from the group including TiO_2 , TrO_2 , TrO_2 , TrO_3 .
- 7. A dental bygiene device, as claimed in claim 5 or 6, wherein said n-type semiconductor bears Pt on a surface thereof.
- 0. A deptal hygione device, as claimed in claim 5 or 6 wherein sold n-type semiconductor boars on a surface thereof any one selected from the group including Ti alloy, any other precious metals then Pt or alloys formed thereof.
- 9. A dental hygheno device, as claimed in claim 5, wherein said n-type semiconductor selected from the group including $T10_2$, $Zr0_2$ and Fe_20_3 is formed by slutering at a high temperature Ti, Zi and Te in the form of powder, respectively.
- 10. A dental hygiene device, as claimed in claim 9, wherein said ${\rm TiO_2}$ is obtained by red-heating Ti at a temperature between 1200 to 1500 $^{\rm O}{\rm C}$ for 2 to 10 minutes.
- 11. A dental hygiene device, as claimed in claim 5 or 6, wherein said n-type semiconductor solected from the group including TiO_3 , KCO_2 and Fe_2O_3 is obtained by an electrolytic oxidation of Ti_1 , Kr_2 , and Fe_2 respectively.

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- 12. A dontal hygiene device, as claimed in claim 1 or 2, wherein said n-type semiconductor is obtained as semiconductor powder used as a new material therefore is treated by a method selected from the group including a pressure moulding, sintering, CVD, vacuum deposition, sputtering and ion plating.
- 13. A deptal hygiene device, as claimed in claim 1 or 2, wherein said inserting portion is formed separately from said grip portion so as to be detachable from the same.
- 14. A dental hygiens device, as claimed in claim 1 or 2, wherein said n-type semiconductor has a leading edge thereof toward said inserting portion disposed adjacent a brush provided at said inserting portion.

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